

# ELASTOMERIC COATING OF FILLER POWDERS BY SLURRY PRECIPITATION

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## Abstract

The work presented here involves the coating of inert particles by an elastomer. The plasticized elastomer is first dissolved in an organic solvent and is mixed with water in which the inert particles are slurried. Due to the miscibility of the organic solvent and water, the elastomer gels and coats the inert particles. The coated particles further coalesce to form the molding powder of desired size range. This paper addresses the dynamics of the coating operation and the role of process parameters on the extent of coating and particle size distribution.

## Introduction

Prior to the processing of energetic formulations, filler powders are often coated with an elastomeric layer to reduce sensitivity for safe handling and ease of processability. One method of accomplishing the coating is to bring into intimate contact the organic solvent in which the elastomer is dissolved and the aqueous solution in which the filler powder is slurried. When water and the organic solvent are miscible in each other, the water functions as an antisolvent since the elastomer is insoluble in water and it gels due to its reduced solubility in the aqueous/organic mixture. The gel adheres to the surface of the filler powder, forming a desensitizing binder layer which further coalesces with other coated powder to form particles (molding powder) of desired size.

In the work presented here, the model powder Dechlorane Plus 515 ( $C_{18}H_{12}Cl_{12}$ ) was slurry coated with cellulose acetate butyrate (CAB) plasticized with BDNPA/F. A mixer vessel was designed where the plasticized CAB (binder), dissolved in ethyl acetate, was metered into the aqueous solution in which the filler powders were suspended. Operating parameters such as temperature, agitation rate, rate of addition of binder solution, suspension density and use of surfactants all affected the size distribution and the integrity of the molding powder. The principal objective of this work was to gain insight into the dynamics of the molding powder

production process and establish the operating conditions for which molding powder of desired size range and uniform binder coating could be obtained.

## Experimental

The experimental setup consisted of the components shown in [Figure 1](#). The mixer is a 1-liter glass vessel with a jacketed aluminum base. A hot water bath provides the circulating water for temperature control. The agitator is pneumatic, run by a 2 HP commercial air compressor with air pressure regulated at 60 psi. An on-line filter is provided to remove moisture and the oil lubricator delivers a controlled quantity of oil to the agitator. Since the agitator is pneumatic and therefore sealed, a non-contact laser tachometer was used to measure and control the agitator rpm. The peristaltic pump is a pre-calibrated variable flowrate pump with a range of 3-80ml/min.

## Materials

The binder was a mix of cellulose acetate butyrate (CAB) and the plasticizer bis-(2,2-dinitropropyl) acetal/formal (BDNPA/F). The binder was solubilized in ethyl acetate.

Dechlorane Plus 515 ( $C_{18}H_{12}Cl_{12}$ ) which is a flame retardant is used as the model powder with a bimodal size distribution as illustrated in [Figure 2](#). n-Butanol was used as a surfactant for the Dechlorane Plus 515 aqueous slurry.

## Background

To our knowledge there is no information in the open literature on the slurry coating where an antisolvent is used to achieve gelation and adherence of the gelled polymer on the solid surface. On the other hand, the use of an antisolvent is common in precipitation processes where solubility of a solute is insensitive to temperature variations (1). In general, it is desired that the two solvents are completely miscible but that the solute is insoluble in

the solvent added. In the present case, although water is only partially miscible with ethyl acetate (solubility of ethyl acetate in water is 9g/100ml at 30 °C), water is an excellent choice as antisolvent because it affords the controlled gelation of the dissolved polymer. Rapid gelation and precipitation which can be achieved with an antisolvent that is completely miscible with ethyl acetate such as an alcohol would not be desirable due to the propensity of the coated powder to agglomerate when large quantities of gel are formed in a short period of time.

Surfactants are typically used to stabilize dispersions (2,3). Here n-butanol plays a key role in preventing Dechlorane powder from agglomerating. However, once the gel adheres on the Dechlorane surface, some agglomeration of the coated Dechlorane is desirable to yield molding powder of average size of about 200 microns.

There is considerable amount of work in the literature on the adsorption of dissolved polymers on solid surfaces (4). The objective in such work is often the stabilization of interfacial systems. Once the polymeric molecules adsorb on the surface, van der Waals attractions and the double-layer repulsion which are the dominant forces of interaction between bare surfaces become very small and the predominant mode of interaction between particles is that of the polymer-polymer overlap. Depending on the nature of interaction of the polymer with the solvent, polymer-polymer interactions can be attractive or repulsive. With a “good” solvent, the polymer molecules are outstretched and the repulsive forces become dominant. With a “bad” solvent the polymer molecule coils in the vicinity of the surface to minimize its contact with the solvent and the attractive forces become important. Such generalizations would also be applicable to the system presently studied although here the adsorbing polymer molecules are in the gel form. Also the desired form of interaction should neither be strong repulsion, in which case the molding powder size will be very small, nor strong attraction, in which case excessive agglomeration will result in large, unusable globules.

## Experimental Procedure

The experiments involved preparing a slurry of Dechlorane powder in water with n-butanol in the 1-liter mixer vessel followed by slow addition of the solution consisting of CAB-BDNPA/F dissolved in ethyl acetate into the vigorously agitated slurry. The operating temperature and rpm were 30 °C and 1000, respectively. The water content and CAB/BDNPA/F solution addition rates were variables.

Immediately after the addition of CAB/BDNPA/F solution, CAB/BDNPA/F gels and starts coating the Dechlorane powder. The coated powder particles

subsequently coalesce to form larger particles. Samples were drawn from the mixer to assess the progress of coating with time. Agitation in the mixer vessel was continued for a duration comparable to that of the CAB/BDNPA/F solution addition time. The mixer contents were then filtered and the particles were dried and analyzed by Scanning Electron Microscopy (SEM) to determine the thickness of coating and the nature of agglomeration. UV-Spectrophotometry was used to determine the amount of binder in the solution as well as the amount on the particles. In the latter case the particles were first contacted with ethyl acetate to dissolve the binder and the amount dissolved was determined with UV-Spectrophotometry. The amount of binder on the particles was also determined gravimetrically.

## Results and Discussions

The analysis of the samples taken every thirty seconds indicated an induction period of approximately 90 seconds during which no coating was observed (Figure 3). Apparently the rate at which the binder continues to adhere to the coated particles is much faster once the first layer of binder is formed on the Dechlorane surface. 90% of CAB/BDNPA/F was found to coat Dechlorane during the first 5 minutes of addition at 10 ml/min. Addition was stopped after five minutes and the total operation time was 10 minutes. It was found that 30-60% of the total CAB/BDNPA/F used was coating Dechlorane, depending on the operating conditions.

The low efficiency of coating prompted the analysis of the water phase for CAB/BDNPA/F. It was found that 28-55% of CAB/BDNPA/F was staying in the water phase at the completion of the process, depending on the experimental conditions. This is a significant finding in view of its economic and environmental ramifications. CAB/BDNPA/F solubility in the water phase is due to its solubility in ethyl acetate, which remains dissolved in the water phase. There is no easy remedy for this problem because the principal mechanism by which CAB/BDNPA/F gels and coats the solids is its lowered solubility due to the miscibility of ethyl acetate and water. Hence, the loss of CAB/BDNPA/F to the water phase is inevitable and, although it can be reduced, it is still significant.

Corresponding to CAB/BDNPA/F addition rate of 10 ml/min, it was found that there is an optimal amount of water for which the loss of CAB/BDNPA/F to the water phase is minimum as illustrated in Figure 4. Figure 5 shows that the amount of binder coating Dechlorane corresponding to the same operating conditions is maximum, as expected.

Based on the microstructural analysis, the best molding powder with uniform grain size and coating

thickness of 0.1-0.2 $\mu\text{m}$  was obtained at the lower CAB/BDNPA/F solution addition rate of 3 ml/min with 400 ml water. Higher addition rates cause binder accumulation in the interparticle spacings and thicker surface coating as well excessive grain agglomeration. Use of more water causes irregularities in binder distribution and lack of grain integrity that results in very small particles. The effect of using less water is similar to using high CAB/BDNPA/F solution addition rates.

Photomicrographs of the molding powder grains typically exhibited hollow-cocoon type structures with sizes ranging from 100-700 $\mu\text{m}$  and CAB/BDNPA/F surface layers of 0.1- 0.5 $\mu\text{m}$  (Figure 6).

The role of n-butanol is crucial for successful production of the molding powder. In the absence of n-butanol, essentially all of the Dechlorane appears as agglomerated froth at the top of the vessel when it is rapidly agitated in an aqueous slurry. n-Butanol acts as a surfactant to break up the froth. 3% n-butanol in water is sufficient to essentially eliminate all the froth. Here, n-butanol, which is a polar molecule, concentrates and orients itself at the solid-liquid interface in such a way that the hydroxyl group is incorporated into the water phase and hydrocarbon group is oriented toward the solid, away from the water (2). By so doing n-butanol reduces the surface tension and prevents agglomeration of the powder.

n-Butanol is also found to hinder the rapid agglomeration of the coated Dechlorane Plus. Hence, it apparently has the same type of steric effect at the polymer-water interface as at the Dechlorane Plus – water interface.

## Acknowledgements

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## Keywords

Coating, slurry precipitation, molding powder.

Figure 1. Molding Powder Process Setup

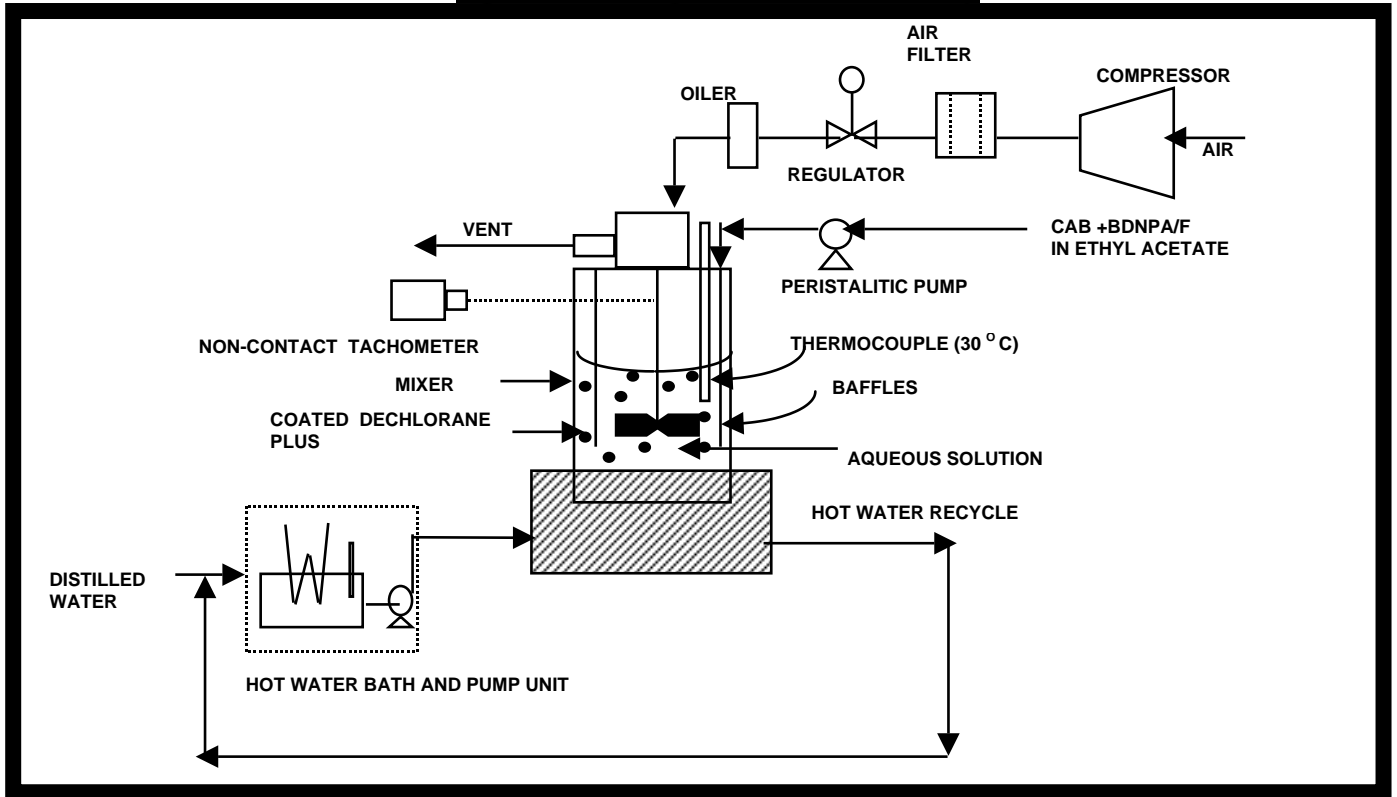


Fig. 2a Dechlorane Plus-515 particles (2000X)

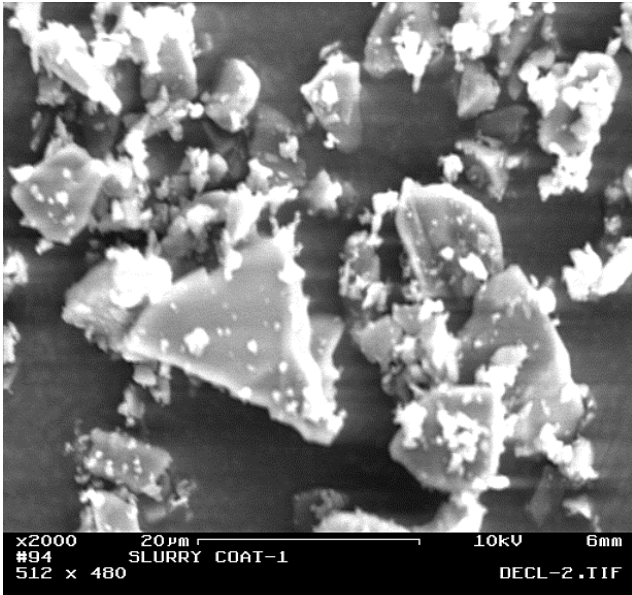
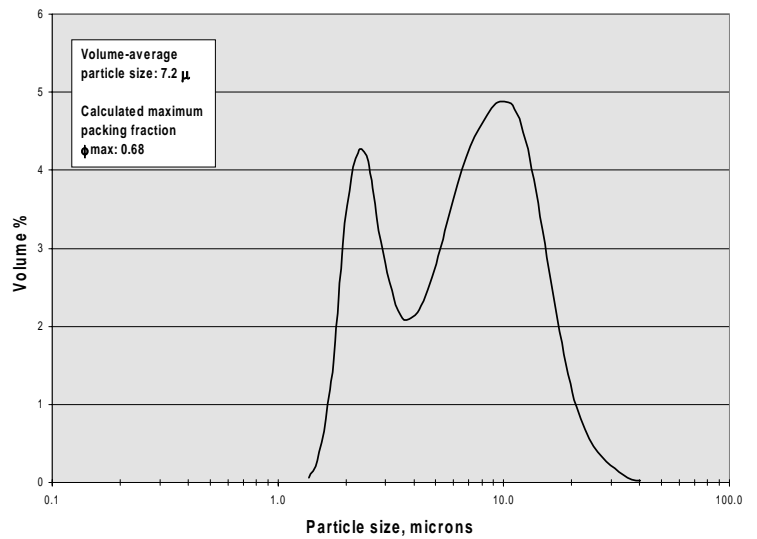
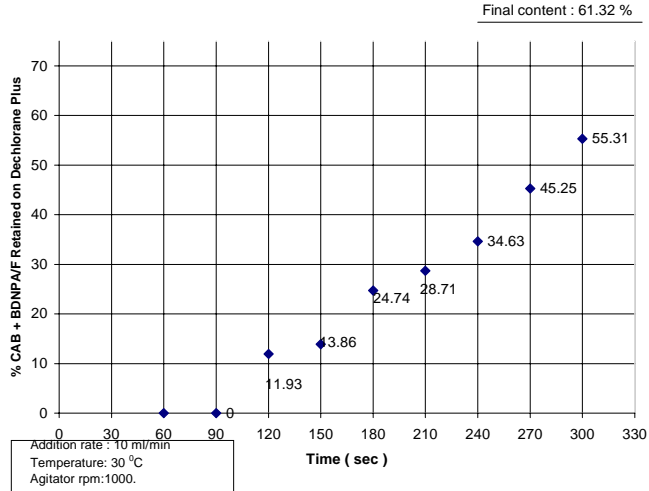


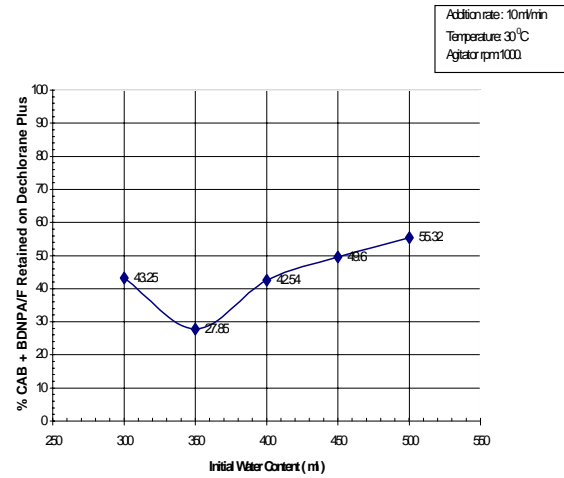
Fig. 2b Particle Size Distribution of Simulant Powder DechloranePlus-515 Measured by Microtrac



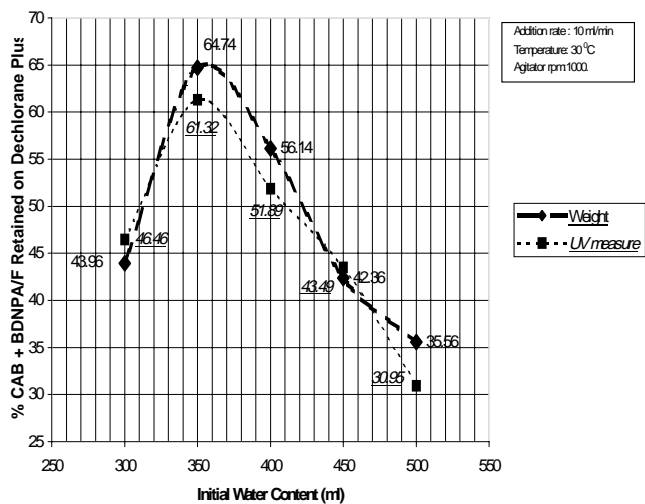
**Figure 3. Variation of CAB + BDNPA/F Coating on Dechlorane Plus.**  
(Initial Water Content = 350 ml)



**Figure4. Variation of CAB+BDNPA/F Content in Aqueous Phase**



**Figure5. Coating of Dechlorane Plus with CAB+BDNPA/F using Gravimetric and UV Spectrophotometry Techniques.**



**Fig. 6 SEM photomicrographs of slurry coated DechloranePlus 515 sample with 10% CAB/BDNPA/F, 400 ml water, 10 ml/min at 50X**

